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(54) IMPROVEMENTS IN AND RELATING TO THE BENEFICATION OF WEATHERED ILMENITE ORE MATERIALS

(71) We, LAPORTE INDUSTRIES LIMITED, a British Company of Hanover House, 14 Hanover Square, London W.1, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the beneficiation of weathered ilmenite ore materials, and is especially concerned with the production from such ilmenites of a material from which the iron content is readily leachable.

Processes for removing the iron values from iron-containing titaniferous material usually involve some form of leaching operation. Indeed, some previously proposed processes involve direct leaching of the ore material itself with a mineral acid under conditions of elevated temperature and pressure. Such processes have the disadvantage that the leaching conditions required to dissolve the iron content of the ore also result in the dissolution of some of the titanium content. The dissolved titanium values are recovered subsequently by precipitation caused by hydrolysis of the residual leach liquor; indeed, according to one previous proposal, the titanium and iron values are both substantially completely dissolved by direct leaching, the titanium values then being recovered by selective precipitation. The precipitate that is obtained from such processes, however, is in a finely divided form, and this renders it unsuitable for conversion into titanium tetrachloride by chlorination under fluidised-bed reaction conditions, which is the process usually carried out on the beneficiated titaniferous material.

The disadvantages of processes involving dissolution and subsequent precipitation of titanium values have led to proposals for processes in which the titaniferous ore material is subjected to a preliminary treatment before

being leached, the purpose of the preliminary treatment being to produce a material having improved leaching characteristics.

A number of previously proposed pre-leaching treatments comprise reducing the ore material to convert at least a part of its iron content into metallic iron. A disadvantage of such processes is that difficulties can arise from sintering of the reduction product. Further, there is a tendency for the titanium dioxide concentrate obtained by leaching the reduction product to break down into undesirably small particles while being chlorinated under fluidised-bed reaction conditions. These drawbacks occur even when, as has been proposed, the reduction step is preceded by an oxidising treatment which converts at least a part of the ferrous iron content of the ore into the ferric state.

Another previously proposed beneficiation process comprises oxidising the titaniferous ore material to convert at least a part of its ferrous iron content into the ferric state, and leaching the oxidised material with aqueous sulphuric acid under reducing conditions and in the presence of inert grinding bodies. The preliminary oxidation may be effected by heating the ore in air to a temperature of from 800° C. to 1350° C.

The present invention provides a process for activating a weathered ilmenite ore material, which comprises subjecting a raw weathered ilmenite ore material to thermal treatment at a temperature in the range of from 600° to 950° C. under conditions which are oxidising or reducing, the thermal treatment being discontinued before the proportion of the iron content of the ore material that has undergone a change in oxidation state exceeds 1/15 by weight, and the thermal treatment being effected under reducing conditions or for a period not exceeding 45 minutes under oxidising conditions provided

by an atmosphere comprising oxygen in a proportion not exceeding 12% by volume.

Where reducing conditions are employed, the duration of the thermal treatment advantageously does not exceed 45 minutes.

Preferably, the ore material is maintained under reducing or oxidising conditions for a period of from 10 to 45 minutes.

When an oxygen-containing atmosphere is used, the proportion of oxygen preferably does not exceed 10%, and it will generally be found that optimum results are obtainable with oxygen contents in the region of 5%, say in the range of from 4 to 7%, by volume.

By subjecting an ilmenite-containing ore material to thermal treatment in accordance with the invention, an activated product is obtained from which a high proportion of the iron content is readily leachable. Further, the beneficiated material obtained after leaching is suitable for use as a feed material for the manufacture of titanium tetrachloride under fluidised-bed reaction conditions. A surprising feature of the process of the invention is that a useful improvement in iron leachability is obtained using relatively short treatment times.

The process of the invention is generally applicable to weathered ilmenite ores such as beach sand ilmenites, alluvial ilmenites, and leucoxenes, and all such materials are "weathered ilmenite ore materials" for the purposes of the present invention. The invention is not concerned with the beneficiation of non-weathered massive ilmenites such as, for example, Norwegian ilmenite and MacIntyre ilmenite.

The raw material that is thermally treated in accordance with the invention is the material obtained by subjecting the natural ore deposit to conventional dressing procedures. Such procedures, which will normally involve magnetic separation and/or flotation treat-

ments, are effective in removing a proportion of the gangue material that contaminates natural ore deposits.

It has been found that, from the point of view of improving the iron leachability of the ore material, it is desirable to restrict the proportion of the iron content that is oxidised or reduced in the course of the thermal treatment.

Advantageously, the conditions during the thermal treatment are such that not more than 1/20 by weight of the iron content of the ore material undergoes any change of oxidation state. In general, thermal treatment under such conditions leads, for a given temperature, to the optimum improvement in the ease of leaching out iron values, as compared with leaching the untreated material, and also as compared with previously proposed processes in which substantially higher proportions of the iron content are oxidised or reduced prior to leaching.

In general, the more strongly oxidising or reducing are the conditions during the thermal treatment, the shorter should be the duration of the treatment at a given temperature, or conversely, the lower should be the temperature for a given treatment duration. These relationships are illustrated in Table 1 which shows, for two different temperature ranges, the maximum concentration of certain gases that may be present (if the fraction of the total iron content undergoing oxidation or reduction is not to exceed 1/15), during a 15 minute thermal treatment of Western Australian beach sand and ilmenite containing from 20 to 25% by weight of ferrous oxide. In the case of each of the six possible gas concentrations given in Table 1, the balance of the atmosphere comprises a chemically inert gas or gases.

TABLE 1

| Temperature Range (°C.) | Maximum gas concentration (% by volume) | | |
|-------------------------|---|-----------------|--------|
| | Hydrogen | Carbon monoxide | Oxygen |
| 650-750 | 7 | 10 | 6 |
| 900-950 | 2 | 2.5 | 2 |

The temperature range that leads to the optimum iron leachability in any given case depends upon the particular ore material that is to be treated.

Thermal treatment in accordance with the invention requires that the titaniferous ore material be maintained for a time at a tem-

perature of from 600° C. to 950° C. If the ore material were to be heated to a temperature significantly above 950° C., or if the material were not to reach a temperature of at least 600° C., a product from which the iron content can readily be removed by leaching would not be obtained.

The reason for the improvement in the ease of leaching out iron values that is obtained by thermal treatment in accordance with the invention is not fully understood. It is believed, however, that the improvement derives from structural changes in the ore material, particularly changes in porosity, brought about by the thermal treatment conditions.

A further benefit deriving from thermal treatment in accordance with the invention is that it leads, in general, to a decrease in the loss of titanium values in the leaching step (and, therefore, to an improvement in titanium dioxide yield), as compared with the results obtained by leaching the untreated ore material. Although the use of oxidising (as opposed to reducing) conditions during the thermal treatment tends to have a slightly detrimental effect on the iron leachability of the product, it will usually be found that such conditions have a favourable effect on the titanium dioxide yield, especially in the case of raw ore materials having a titanium dioxide content of less than 60% by weight, more especially less than 56% by weight. For such ores, thermal treatment in an oxygen-containing atmosphere in accordance with the invention gives an activated product having good leaching characteristics both in terms of iron leachability and in terms of titanium dioxide yield.

It is essential that, when the thermal treatment is carried out under oxidising conditions, the oxygen content of the surrounding atmosphere should not exceed 12% by volume. If,

a higher concentration of oxygen were to be present, the improved iron leachability deriving from thermal treatment would not be obtained. The reason for this is not fully understood, but it is believed that, when the thermal treatment of the invention involves oxidation, the conditions must be such that the rate of the thermally-induced structural change is significantly faster than the rate of oxidation of the iron values. Further, it will generally be found that the maximum desirable oxygen concentration will be lower, the higher is the temperature that is to be employed in the thermal treatment.

The titanium dioxide yield on leaching may also be further improved by carrying out an oxidative treatment after first subjecting the ore material to thermal treatment under reducing conditions in accordance with the invention, that is to say, under conditions which are such that not more than 1/15 of the iron content is reduced. It will generally be found, however, that little or no advantage is gained from such oxidative treatment when the initial titanium dioxide content of the raw ore material exceeds 56% by weight, and especially where it exceeds 60% by weight. Titanium dioxide contents in those ranges are usually found in relatively highly weathered ores, for example, leucoxenes, Quilon and Secondary Western Australian ilmenites.

As will be appreciated by those skilled in the art, the % TiO_2 Yield on leaching is calculated from:

Weight of TiO_2 in Product produced from Given Weight of Feed Ore

Weight of TiO_2 in a Given Weight of Feed Ore

$\times 100\%$

In those cases in which there is room for effecting a worthwhile improvement in titanium dioxide yield by carrying out an oxidative treatment after reduction thermal treatment according to the invention, the thermally-treated material may be oxidised until substantially all of the iron values are in the ferric state, but it is preferably to oxidise a part only of the ferrous iron content. Advantageously the thermally-treated material is oxidised until approximately one-half of its ferrous oxide content (calculated as FeO by weight) has been converted into the ferric state.

Conveniently, oxidative treatment following thermal treatment is effected by contacting the thermally-treated material with air at a temperature in the range of from 700° — 850° C. Higher temperatures may be used, but care should be taken to restrict pseudobrookite formation as far as possible, otherwise the material will become progressively more difficult to leach.

The fact that beneficial results generally

follow from carrying out an oxidative treatment after thermal treatment has the additional advantage that steps need not be taken to avoid atmospheric oxidation while a thermally-treated ore material is cooling down prior to leaching. This is in clear contrast with those previously proposed processes that involve a reduction step immediately prior to leaching. In such processes, undesirable results generally follow unless steps are taken to prevent re-oxidation prior to leaching.

Although it is sometimes advantageous to oxidise an ore material after it has been subjected to thermal treatment under reducing conditions in accordance with the invention, it should be noted that no significant advantage is gained by carrying out a reducing thermal treatment after completing a thermal treatment in an oxygen atmosphere in accordance with the invention.

Thermal treatment in accordance with the invention may be carried out in any suitable apparatus, for example, in a rotary kiln or in a fluidised-bed apparatus. The desired tem-

perature in the range of from 600° to 950° C. may be attained by burning in air a fuel such as, for example, oil, town gas, natural gas, oil refinery tail gas, or a similar combustible material. Care should be taken to ensure that any excess of air supplied to the burners does not result in the oxygen content of the atmosphere surrounding the ore material exceeding 12% by volume.

An oxidising treatment effected following a reducing thermal treatment according to the invention may also be carried out in a rotary kiln or in a fluidised-bed apparatus. Advantageously, such an oxidising treatment is carried out by contacting the thermally-treated material with preheated air under fluidised-bed conditions.

Leaching may be effected with any mineral acid, but it is preferable to use hydrochloric acid, which may be recovered from the residual leach liquor by a thermal decomposition process, for example, by the process disclosed in British Patent Specification No. 793,700.

Preferably, the leaching is effected at normal atmospheric pressure and the acid strength is in the range of from 17.5 to 25% w/w. If desired, the leaching may be effected under superatmospheric pressure, and acid having a somewhat lower strength may then be used. Typically, when hydrochloric acid is used having a concentration of from 17.5 to 25% w/w, the optimum iron removal will be brought about at a residence or contact time of from 5 to 9 hours at temperatures exceeding 100° C.

Advantageously, there is used an excess of acid in the range of from 25% to 75% over the stoichiometric quantity required in respect of the iron values only. Leaching is advantageously effected at a temperature of at least 100° C. and is preferably effected at the boiling temperature of the leaching solution.

The leaching treatment may be effected batch-wise or as a continuous process. Advantageously, when a continuous leaching process is used, the process is operated counter-current. The leaching treatment may be carried out in a stirred vessel or vessels, but is advantageously carried out under fluidised conditions. Such conditions give rise to improved solid/liquid contact and, as a result, more efficient iron removal and higher yields are achieved, as compared with stirred systems.

Preferably, the acid leaching solution contains some ferrous iron initially; for example, a solution of ferrous chloride in hydrochloric acid may be used. In general, such a solution will produce similar results in terms of titanium dioxide yield and iron removal to those obtained by using the same quantity of acid alone, but the leaching will be complete in a significantly shorter time. Advantageously, the acid leaching solution contains recycled leach liquor.

After being leached, the material will be washed to remove residual leach liquor, and then dried. Advantageously, the material is dried by being calcined to a temperature of from 600° to 700° C., preferably for a period of from $\frac{1}{2}$ to 2 hours, and especially for about $\frac{1}{2}$ hour. The calcination may be effected in any suitable apparatus.

Calcination of leached material to 600°—700° C. enhances the reactivity of the material when it is subsequently chlorinated under fluidised-bed reaction conditions. For this purpose, the reactivity of the calcined material is measured by evaluating the ratio $\text{CO}/(\text{CO} + \text{CO}_2)$ for the exhaust gases from the chlorinator. The value of this ratio provides a measure of the exothermicity of the chlorination reaction, and a low value of the ratio is taken to indicate a highly reactive material. It should be noted that, in practice, the value for the ratio is taken as the mean of a number of readings made during the chlorination process. The carbon monoxide and carbon dioxide contents of the exhaust gases from the chlorinator may be determined by gas-liquid chromatography.

It is a feature of the process of the invention that the magnetic susceptibility of the ore material is increased by the thermal treatment, and this enables magnetic separation techniques to be employed at various stages. Advantageously, the thermally-treated ore material is subjected to a magnetic separation technique before being acid leached. The non-magnetic and/or weakly magnetic material removed in this way contains a high proportion of substances, for example, siliceous materials, which are not dissolved during leaching. By carrying out a magnetic separation prior to leaching, the titanium dioxide content of the beneficiate ultimately obtained may be increased by up to 3%. A useful improvement is also obtained if, instead of effecting magnetic separation before leaching, such a separation is performed on the material after leaching.

The following expression is to be used in calculating the fraction of the total iron content that has been oxidised during a thermal treatment in accordance with the invention:

$$(X_1 - X_2) \times 56/72 \times 1/Z_1$$

where X_1 is the percentage by weight of ferrous iron (calculated as FeO) in the starting material;

X_2 is the percentage by weight of ferrous iron (calculated as FeO) in the material after thermal treatment; and

Z_1 is the total iron content of the starting material (expressed as a percentage by weight and calculated as Fe).

In the case of thermal treatment under reducing conditions, the fraction of the total

70

75

80

85

90

95

100

105

110

115

120

125

iron content that has been reduced is to be calculated by the expression:

$$(X_2 - X_1) \times 56/72 \times 1/Z_1$$

in which the symbols X_1 , X_2 , and Z_1 are as hereinbefore defined.

It will be appreciated that a consequence of the restriction of reduction to a maximum of 1/15 iron conversion is that there will be negligible formation of metallic iron, which is therefore omitted from the above expression.

TABLE 2

(Example 1 below)

| Product | Product Analysis | | TiO ₂ Yield | Iron Removal |
|---------|------------------------|----------------|------------------------|--------------|
| | % w/w TiO ₂ | % w/w Total Fe | % | % |
| R | 74.9 | 16.0 | 93.7 | 63.4 |
| Q | 85.0 | 9.1 | 95.5 | 81.4 |

The following Examples illustrate the invention:

Example 1.

100 gm. of a Western Australian ilmenite was thermally treated in a fluidised bed for 30 minutes at 850° C. in an atmosphere comprising 97.5% nitrogen and 2.5% oxygen. The thermally-treated material was found to contain 20.8% by weight of ferrous iron calculated as FeO, and it was calculated that less than 1/15 of the initial iron content of the ore (calculated as Fe) had been oxidised. After cooling, the thermally treated material was leached for 7 hours using a 50% excess of 20% hydrochloric acid at boiling temperature. The leached material was separated from the residual leach liquor, and was then washed thoroughly to remove entrained leach liquor.

After washing, the material was dried at 700° C. for 30 minutes to give a product Q.

In order to provide a basis for comparison with Example 1, 100 gm. of the same Western Australian ilmenite was leached directly for 7 hours with a 50% excess of boiling hydrochloric acid, with no preliminary thermal treatment. The leached product was washed and dried as described in the Example to give a product R.

The titanium dioxide and total iron contents of the products Q and R, together with the calculated yield and iron removal data, are given in Table 2.

The percentage yield of titanium dioxide was calculated using the expression given hereinbefore, and the percentage iron removal was calculated as follows:

$$\% \text{ iron removal} = \frac{W(\text{feed}) - W(\text{product})}{W(\text{feed})} \times 100$$

where $W(\text{feed})$ = weight of iron in feed material; and $W(\text{product})$ = weight of iron in product.

Example 2.

250 Gm. samples of a Western Australian beach sand ilmenite were subjected to thermal treatments under the conditions shown in the Table below. After being cooled, 100 gm. of each thermally treated material was leached for 7 hours using a 50% excess of 20% w/w hydrochloric acid under boiling condi-

tions. The leached product was washed to remove residual leach liquor, and was then dried at 700° C. for 30 minutes. The dry product was weighed and analysed for TiO₂ content, and the Table below shows both the TiO₂ content and the calculated TiO₂ yield in each case.

It will be seen that the results obtained by thermal treatment in an atmosphere having an oxygen content of 5% are superior, both in terms of titanium dioxide yield and in terms of iron leachability, to those obtained using oxygen contents of 2.5% or 7.5%.

TABLE

| Atmosphere | | Time (min.) | Temperature (°C) | Percentage TiO ₂ | TiO ₂ Yield |
|----------------|----------------|----------------|---------------------|--------------------------------|---------------------------|
| O ₂ | N ₂ | | | | |
| 2.5 | 97.5 | 5 | 800 | 83.1 | 92.9 |
| 5.0 | 95.0 | 5 | 800 | 85.5 | 98.3 |
| 7.5 | 92.5 | 5 | 800 | 82.0 | 95.4 |

WHAT WE CLAIM IS:—

1. A process for activating a weathered ilmenite ore material, which comprises subjecting a raw weathered ilmenite ore material to thermal treatment at a temperature in the range of from 600° to 950° C. under conditions which are oxidising or reducing, the thermal treatment being discontinued before the proportion of the iron content of the ore material that has undergone a change in oxidation state exceeds 1/15 by weight, and the thermal treatment being effected under reducing conditions or for a period not exceeding 45 minutes under oxidising conditions provided by an atmosphere comprising oxygen in a proportion not exceeding 12% by volume.
2. A process as claimed in claim 1, wherein the duration of the thermal treatment is at least 10 minutes.
3. A process as claimed in claim 1 or claim 2, wherein the oxygen content of the atmosphere during the thermal treatment does not exceed 10% by volume.
4. A process as claimed in claim 3, wherein the said oxygen content is in the range of from 4 to 7% by volume.
5. A process as claimed in any one of claims 1 to 4, wherein the titanium dioxide content of the raw ore material is 60% by weight or less, and the thermal treatment is conducted under oxidising conditions.
6. A process as claimed in claim 5, wherein the titanium dioxide content of the raw ore material is 56% by weight or less, and the thermal treatment is conducted under oxidising conditions.
7. A process as claimed in claim 1 or claim 2, wherein the thermal treatment is conducted under reducing conditions for a period not exceeding 45 minutes.
8. A process as claimed in any one of claims 1 to 7, wherein not more than 1/20 by weight of the iron content of the ore material undergoes any change of oxidation state during the thermal treatment.
9. A process as claimed in any one of claims 1, 2 or 7, wherein the ore material is subjected to an oxidative treatment after the said thermal treatment.
10. A process as claimed in claim 9, wherein substantially all of the iron values of the ore material are in the ferric state after said oxidative treatment.
11. A process as claimed in claim 9, wherein the oxidative treatment converts a part only of the ferrous iron content of the thermally treated material to the ferric state.
12. A process as claimed in claim 11, wherein approximately one half by weight of the ferrous iron content of the thermally treated material is converted to the ferric state during the oxidative treatment.
13. A process as claimed in any one of claims 9 to 12, wherein the said oxidative treatment comprises contacting the thermally treated material with air at a temperature in the range of from 700° to 850° C.
14. A beneficiation process comprising an activation process as claimed in any one of claims 1 to 8, followed by acid leaching of the thermally-treated material.
15. A beneficiation process comprising an activation process as claimed in any one of claims 9 to 13, followed by acid leaching of the material resulting from the said oxidative treatment.
16. A process as claimed in claim 14 or claim 15, wherein leaching is effected by means of a mineral acid.
17. A process as claimed in claim 16, wherein the mineral acid comprises hydrochloric acid.
18. A process as claimed in any one of claims 14 to 17, wherein the strength of the acid leachant is in the range of from 17.5 to 25% w/w.
19. A process as claimed in any one of claims 14 to 18, wherein there is used an excess of acid leachant in the range of from 25% to 75% over the stoichiometric quantity calculated in respect of iron values only.
20. A process as claimed in any one of claims 14 to 19, wherein the leaching is effected at a temperature of at least 100° C.
21. A process as claimed in any one of claims 14 to 20, wherein leaching is effected at the boiling temperature of the leachant.
22. A process as claimed in any one of claims 14 to 21, wherein the leaching is effected as a continuous counter-current process.
23. A process as claimed in any one of

- claims 14 to 22, wherein the leaching is effected under fluidised conditions.
24. A process as claimed in any one of claim 14 to 23, wherein the leachant solution contains some ferrous iron initially.
25. A process as claimed in any one of claims 14 to 24, wherein the leachant includes recycled leach liquor.
26. A process as claimed in any one of claims 14 to 25, wherein the leached material is calcined to a temperature of from 600° to 700° C.
27. A process as claimed in claim 26, wherein the calcination is continued for a period of from $\frac{1}{4}$ to 2 hours.
28. A process as claimed in claim 27, wherein the calcination is continued for a period of $\frac{1}{2}$ hour.
29. A process as claimed in any one of claims 14 to 28, wherein the thermally treated ore material is refined by a magnetic separation technique before being leached.
30. A process as claimed in any one of claims 1 to 29, wherein the weathered ilmenite ore material comprises a beach sand ilmenite, an alluvial ilmenite, or a leucoxene.
31. A process as claimed in claim 14, for beneficiating a weathered ilmenite ore material, conducted substantially as described in any one of the Examples herein.
32. A readily leachable titaniferous material whenever obtained by a process as claimed in any one of claims 1 to 13, or in claim 30 as appended thereto.
33. A beneficiated titaniferous material whenever obtained by a process as claimed in claim 31, or in any one of claims 14 to 29, or in claim 30 as appended thereto.
34. A process for the manufacture of titanium tetrachloride, which comprises chlorinating under fluidised-bed reaction conditions a material as claimed in claim 33.
35. Titanium tetrachloride whenever prepared by process as claimed in claim 34.
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